An Investigation of HDDR Phenomena in the $\text{Sm}_3(\text{Fe},\text{V})_{29}$ Compound

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Hydrogenation, Disproportionation, Desorption, Recombination (HDDR) phenomena have been studied in the new magnetic phase, $\text{Sm}_3(\text{Fe},\text{V})_{29}$. Samples of $\text{Sm}_3(\text{Fe},\text{V})_{29}$ were HDDR treated at various temperatures, from 700°C to 950°C. XRD measurements showed that the samples did not recombine into $\text{Sm}_3(\text{Fe},\text{V})_{29}$, but rather, recombined into a mixture of a TbCu_7 type phase and $\alpha\text{-Fe(V)}$. An extra XRD peak was observed after HDDR at 950°C and it is possible that this extra peak can be attributed to $\text{Sm}_2(\text{Fe},\text{V})_{17}$, since heating $\text{Sm}_3(\text{Fe},\text{V})_{29}$ directly to 1100°C under hydrogen, results in recombination into $\text{Sm}_2(\text{Fe},\text{V})_{17}$ and $\alpha\text{-Fe(V)}$. Material with an intrinsic coercivity of 580kAm⁻¹ (7.3kOe) was obtained after HDDR treatment at 800°C and nitrogenation at 560°C for 4 hours.

*Keywords: HDDR, nitrogenation, $\text{Sm}_2(\text{Fe},\text{V})_{17}$, TbCu_7 type, $\text{Sm}_3(\text{Fe},\text{V})_{29}$,
disproportionation reaction, recombination reaction*

I. Introduction

After Takeshita and Nakayama⁽¹⁾ showed that coercive powder could be produced by heating Nd-Fe-B under hydrogen and then vacuum annealing, Harris et al.⁽²⁾ interpreted this behaviour in terms of what they termed a Hydrogenation, Disproportionation, Desorption, Recombination (HDDR) reaction. The $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase disproportionates, under hydrogen at high temperatures, into an intimate mixture of $\alpha\text{-Fe}$, Nd hydride and Fe_2B , which, under vacuum heat treatment, recombines into $\text{Nd}_2\text{Fe}_{14}\text{B}$, but with a greatly reduced grain size. The HDDR process has proved to be a valuable technique for obtaining coercive Nd-Fe-B powder⁽³⁾, and efforts are now being made to develop and scale up the process⁽⁴⁾.

Work in this laboratory, showed that HDDR phenomena could also be applied to other R-Fe (where R = Rare-earth) based alloys, such as $\text{Sm}_2\text{Fe}_{17}$ ^(5,6) and $\text{Nd}(\text{Fe},\text{M})_{12}$ ⁽⁷⁾, to give powders with appreciable coercivity, after nitriding.

Recently, Collocott et al.⁽⁸⁾ reported a new intermetallic compound which has been shown to have a monoclinic structure and a composition of $\text{R}_3(\text{Fe},\text{M})_{29}$ (where M = Transition metal)^(9,10). The composition lies between the 1:12 and 2:17 phases, and can be viewed as an alternating stack of 1:12 and 2:17 units⁽⁹⁾. As with R_2Fe_{17} compounds, nitriding greatly improves the magnetic properties, and in particular, $\text{Sm}_3(\text{Fe},\text{M})_{29}\text{N}_x$ is a very promising alloy for permanent magnets⁽¹¹⁾.

Therefore, the aim of this work was to investigate the effect of HDDR phenomena on the $\text{Sm}_3(\text{Fe},\text{V})_{29}$ phase. Based on a detailed study of the Sm-Fe-V ternary system, carried out within this laboratory⁽¹²⁾, an alloy of composition $\text{Sm}_{9.4}\text{Fe}_{84.6}\text{V}_{6.0}$, was selected as suitable for obtaining near single phase $\text{Sm}_3(\text{Fe},\text{V})_{29}$.

II. Experimental Procedure

An alloy of composition $\text{Sm}_{9.4}\text{Fe}_{84.6}\text{V}_{6.0}$ was induction melted from Sm (99.96% purity), Fe (99.9%), and ferro-vanadium (52.3% by mass V, with the balance Fe), under an Ar atmosphere, and then homogenized at 1150°C for 20 hours. X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM) (with energy dispersive X-ray spectroscopy (EDX)), confirmed that the alloy was nearly single phase $\text{Sm}_3(\text{Fe},\text{V})_{29}$ with a small amount of $\alpha\text{-Fe(V)}$.

The homogenized alloy was ground into a powder, sieved to a particle size less than 63 μm , and pressed into green compacts. These 5g compacts were used to investigate the hydrogen absorption and desorption characteristics, and to produce HDDR treated, and nitrided HDDR samples.

The hydrogen absorption and desorption characteristics were measured by monitoring the difference in flow rate of hydrogen entering (200cm³min⁻¹) and exiting the furnace (denoted as ΔQ). A more detailed description of this technique has been given by Nakamura et al.⁽⁶⁾. Samples were obtained at certain temperatures, by heating under hydrogen and quenching in argon (hereafter referred to as the "H treatment"), as shown in Fig.1(i), to investigate the nature of the different absorption / desorption events. The purpose of the Ar heat treatment was to ensure that all the hydrogen was flushed from the furnace, and to prevent the formation of other phases, such as SmH_3 , upon cooling.

HDDR samples were obtained following the procedure shown in Fig.1(ii), using treatment temperatures from 750 to 950 °C. Part of the HDDR samples were then nitrided from 520 to 560°C for 4 hours.

In addition, 800°C HDDR treated samples were heated in nitrogen, to temperatures between 520 to 600°C for 4 hours, in order to investigate the effect of nitrogenation temperature.

Nitrided HDDR samples were ground into powder, which was mixed with molten paraffin that solidified within a magnetic field of 1.0 MA m^{-1} (1.2T). The magnetic properties were measured using a vibrating sample magnetometer (VSM) with a maximum applied magnetic field of 1.2 MA m^{-1} (1.5T), after applying a pulsed field of 4.0 MA m^{-1} (5.0T) to the sample.

X-ray diffraction (XRD) was performed on a computerised step-scan diffractometer, using Fe-K α radiation.

Fig.1 Schematic diagrams of (i) the heat treatment in hydrogen and (ii) the HDDR treatment. H_2 and Ar gas flows were $200 \text{ cm}^3/\text{min}$.

III. Results and Discussion

The hydrogen absorption and desorption characteristics of the $\text{Sm}_{9.4}\text{Fe}_{84.6}\text{V}_{6.0}$ alloy are shown in Figure 2. There are two prominent exothermic absorption peaks which are centred at 295 and 660°C . The first peak can be attributed to the formation of $\text{Sm}_3(\text{Fe,V})_{29}$ hydride; Ryan et al.⁽¹³⁾ reported that $\text{Nd}_3(\text{Fe,Ti})_{29}$ readily hydrides to form $\text{Nd}_3(\text{Fe,Ti})_{29}\text{H}_{6.1}$ after heating in H_2 to 300°C . The second peak is due to the disproportionation of the $\text{Sm}_3(\text{Fe,V})_{29}$ phase into $\alpha\text{-Fe(V)}$ and Sm hydride, as shown by the XRD pattern in Figure 3 of a sample heated to 720°C (a in Figure 2). The broad endothermic peak between these two events is associated with the gradual desorption of hydrogen as the $\text{Nd}_3(\text{Fe,Ti})_{29}$ hydride reverts to $\text{Nd}_3(\text{Fe,Ti})_{29}$. In the case of $\text{Nd}_2\text{Fe}_{14}\text{B}$ ⁽¹⁴⁾ and $\text{Sm}_2\text{Fe}_{17}$ ⁽¹⁵⁾ heated under hydrogen, the hydride phases have dissociated at the onset of the disproportionation reaction. The XRD peaks associated with Sm hydride appear to be rather broad, which Christodoulou and Takeshita⁽¹⁶⁾, in the case of disproportionated $\text{Sm}_2\text{Fe}_{17}$, attributed to a combination of microcrystallinity and to the non-stoichiometric nature of the hydride.

After further heating, two endothermic desorption peaks were observed; a small peak centred at 975°C and a larger one at 1065°C . The larger peak is due to the dissociation of the Sm hydride and, according to the XRD pattern (Figure

3) of a sample heated to 1150°C (c in Figure 2), the subsequent recombination into $\text{Sm}_2(\text{Fe,V})_{17}$. A significant amount of $\alpha\text{-Fe(V)}$ is also present. The cause of the peak at 975°C , however, is not so clear. The XRD pattern (Figure 3) of a sample heated to 1015°C , between the two peaks (b in Figure 2), shows what appears to be an intermediate state with the presence of $\text{Sm}_2(\text{Fe,V})_{17}$, Sm hydride and $\alpha\text{-Fe(V)}$. However, it should be noted that with the close proximity of the two high temperature events, it is difficult to ensure that the sample obtained is totally representative of the narrow region between the peaks. In addition, holding the sample for the 0.1 hours under Ar at the H treatment temperature (Figure 1(i)) may cause a small amount of grain growth.

Fig.2 The hydrogen absorption and desorption characteristics of $\text{Sm}_{9.4}\text{Fe}_{84.6}\text{V}_{6.0}$.

Fig.3 XRD patterns of as homogenized $\text{Sm}_{9.4}\text{Fe}_{84.6}\text{V}_{6.0}$ alloy and after H treatment (figure 1(i)) at (a) 720°C , (b) 1015°C and (c) 1150°C .

In another rare-earth transition metal based system, Nd-Fe-B, Book and Harris⁽¹⁴⁾ attributed a double peak observed during the recombination under vacuum of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase in high Nd content alloys, to a difference in the rate of dissociation of NdH_2 in the disproportionated mixture and NdH_2 at the grain boundaries. However, in this study, the $\text{Sm}_3(\text{Fe,V})_{29}$ alloy is slightly Fe rich, and no Sm-rich phases were observed by SEM analysis. Unidentified double peaks have also been observed during the high temperature recombination of disproportionated $\text{NdFe}_{10}\text{V}_2$ alloy⁽⁷⁾.

One possibility is that a small amount of undetected $\text{Sm}_2(\text{Fe,V})_{17}$ was present in the as homogenized alloy, and

Fig.4 XRD patterns of $\text{Sm}_{9.4}\text{Fe}_{84.6}\text{V}_{6.0}$ HDDR treated at temperatures from 750 to 950°C.

Fig.5 XRD patterns of $\text{Sm}_{9.4}\text{Fe}_{84.6}\text{V}_{6.0}$ HDDR treated at temperatures from 750 to 950°C, and then nitrided for 4 hours at 540°C.

that after disproportionation, it recombined back into $\text{Sm}_2(\text{Fe,V})_{17}$, but at a slightly lower temperature. However, there is no evidence to confirm this theory at present.

The HDDR process was applied to $\text{Sm}_{9.4}\text{Fe}_{84.6}\text{V}_{6.0}$ by heat treating the alloy under hydrogen and vacuum, according to the schematic diagram in Figure 1 (ii). The XRD patterns in Figure 4 show that for HDDR treatment temperatures between 750-950°C, a TbCu_7 type phase forms and not $\text{Sm}_3(\text{Fe,V})_{29}$. The XRD spectra are remarkably similar over the processing temperature range from 750°C to 950°C, with the exception of a single peak that begins to emerge at higher temperatures (denoted by X in Figure 4). Since, as was shown in Figure 3, $\text{Sm}_2(\text{Fe,V})_{17}$ forms at high temperatures, we may tentatively ascribe this peak to the formation of $\text{Sm}_2(\text{Fe,V})_{17}$.

Figure 5 shows the XRD profiles of samples that were nitrided at 540°C for 4 hours, after HDDR treatment. There is a shift in the TbCu_7 type peaks consistent with the formation of a nitride phase. The extra peak seen at high temperatures in the HDDR samples (X in Figure 4) is again present (Y in Figure 5) and also appears to have shifted due to nitrogenation, which suggest that the peak is certainly due to a nitride forming phase.

VSM measurements were made on samples HDDR treated from 750-950°C, and then nitrided for 4 hours at temperatures between 520°C and 560°C. Coercivity against HDDR treatment temperature is plotted in Figure 6, and the maximum coercivity was found to be at 800°C for all of the nitriding temperatures. The presence of this maximum may be attributed to the establishment of an optimum microstructure so that in the lower temperature regime the coercivity is degraded by the presence of soft ferromagnetic free iron, whereas at higher temperatures it is limited by the presence of easily demagnetised large grains, as has been shown for HDDR in other R-Fe based alloys^(2,3,5).

Fig.6 The effect of HDDR and nitrogenation treatment temperatures on the coercivity of nitrided HDDR $\text{Sm}_{9.4}\text{Fe}_{84.6}\text{V}_{6.0}$ samples.

IV. Conclusions

The $\text{Sm}_3(\text{Fe,V})_{29}$ compound disproportionates into $\alpha\text{-Fe(V)}$ and Sm hydride, when heated in hydrogen to about 660°C . After further heating in hydrogen, the disproportionated mixture recombines into $\text{Sm}_2(\text{Fe,V})_{17}$ at about 1065°C , with a significant amount of $\alpha\text{-Fe(V)}$ remaining.

However, HDDR treatment at temperatures between 750 and 950°C leads to the recombination of a TbCu_7 type phase. At higher HDDR temperatures (900 and 950°C) an additional XRD peak was observed, and this has been tentatively ascribed to the formation of $\text{Sm}_2(\text{Fe,V})_{17}$.

The highest coercivity material, 580kAm^{-1} (7.3kOe), was obtained after HDDR treatment at 800°C and nitrogenation for 4 hours at 560°C .

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Fig. 7 The effect of nitrogenation treatment temperature on the coercivity of $\text{Sm}_{9.4}\text{Fe}_{84.6}\text{V}_{6.0}$ samples HDDR treated at 800°C .

The highest coercivity material was obtained at a nitriding temperature of 560°C (Figure 6). In order to ascertain whether this could be further improved, samples were prepared at higher nitriding temperatures using the 800°C HDDR treated material. The results are plotted as coercivity against nitriding temperature in Figure 7, and they confirm that the optimum nitrogenation temperature is about 560°C , with a maximum coercivity of 580kAm^{-1} (7.3kOe). The increase in magnetization and decrease in coercivity at higher nitriding temperatures, shown in Figure 8, may be attributed to the formation of $\alpha\text{-Fe(V)}$, caused by the disproportionation of the TbCu_7 type phase under nitrogen, as has been observed during the nitrogenation of $\text{Sm}_2\text{Fe}_{17}$ ⁽⁵⁾.

Fig. 8 The effect of nitrogenation temperature on the magnetization (at 1.2MAm^{-1}) and remanent magnetization of $\text{Sm}_{9.4}\text{Fe}_{84.6}\text{V}_{6.0}$ samples, HDDR treated at 800°C .